

NON-LORENTZIAN ION CYCLOTRON RESONANCE LINE  
SHAPES ARISING FROM VELOCITY-DEPENDENT  
ION-NEUTRAL COLLISION FREQUENCIES\*

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Abstract

An asymptotic solution of the Boltzmann equation is developed for ICR absorption, without restrictions on the ion-neutral collision frequency or mass ratio. Velocity dependence of the collision frequency causes deviations from Lorentzian line shape.

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## 1. Introduction

Most of the work on the theory of ion cyclotron resonance (ICR) absorption spectra has been restricted to the case of velocity-independent ion-neutral collision frequencies (Maxwell model), or has involved the essentially equivalent assumption that the average of a product is equal to the product of the averages [1-6]. These theories all yield Lorentzian line shapes for the steady-state absorption in a weakly ionized gas, provided that the effects of walls and chemical reactions can be ignored, and that the collision frequency is much less than the cyclotron frequency. The Maxwell-model restriction has been removed for electron absorption, but only at the cost of the new restriction of ion mass much less than neutral mass (Lorentz model) [7,8]. For this model it was found that the line shape depended strongly on the velocity dependence of the collision frequency. The problem could also be solved for the special case of ion mass much greater than neutral mass (Rayleigh model) [9], but, as shown below, the line shape will again be Lorentzian.

The purpose of this communication is to lift the restrictions on ion-neutral collision frequency and mass ratio, so that deviations from Lorentzian line shape can be interpreted in terms of the nature of the ion-neutral force law.

## 2. Theory and Results

The fundamental assumption is that the ion density,  $n$ , is much less than the density of neutral gas molecules,  $N$ , so that ion-ion collisions can be neglected compared to ion-neutral collisions. The collision term of the Boltzmann equation then becomes linear, and can be expanded in a series and the resulting equations solved by a moment method [10,11], without restrictions on collision frequency or mass

ratio. In order to illustrate the dependence of the ICR line shape on the ion-neutral force law, we consider a very simple situation. Ion-neutral collisions are assumed elastic. A uniform static magnetic field  $\underline{B}$  points in the y-direction, and a uniform alternating electric field  $\underline{E} = E_0 \sin \omega t$  points in the z-direction. The ion density is assumed uniform so that boundaries are neglected, and the ion-neutral collision frequency is assumed small compared to the cyclotron frequency  $\omega_c = qB/m$ , where  $q$  and  $m$  are the charge and mass of the ion. Finally, we seek only a steady-state solution, so that we can neglect the initial conditions of the ions, which decay exponentially in time. The theory is not limited to this specialized situation, and the foregoing restrictions can be relaxed (except for  $n \ll N$  and elastic collisions), although at the price of some additional mathematical complication.

Solutions of the linearized Boltzmann equation can be obtained by expanding the collision operator in terms of a complete set of orthogonal functions and forming moments [10]. We use the Burnett functions, the eigenfunctions of the collision operator for the Maxwell model,

$$\psi_{\ell m}^{(r)} = c^\ell S_{\ell+1/2}^{(r)}(c^2) P_\ell^{|m|}(\cos \theta) e^{im\phi}, \quad (1)$$

$$c = v (m/2kT)^{1/2}, \quad \cos \theta = c_z/c, \quad (2)$$

where  $S_{\ell+1/2}^{(r)}$  is a Sonine polynomial,  $P_\ell^{|m|}$  an associated Legendre polynomial,  $v$  the ion velocity, and  $T$  the neutral gas temperature. The infinite set of moment equations must be solved by some truncation and iteration procedure; using the scheme in [11,12] we obtain for the p-th approximation the expression,

$$\left[ \frac{\partial}{\partial t} + N b_{rr}(\ell_m) \right] \left\langle \psi_{\ell_m}^{(r)} \right\rangle_p = \frac{q}{m} \left( \frac{m}{2kT} \right)^{1/2} \left[ E_{\omega 0} \cdot \left\langle \nabla_c \psi_{\ell_m}^{(r)} \right\rangle_p + \right. \\ \left. + \left\langle (\nabla \times B) \cdot \nabla_c \psi_{\ell_m}^{(r)} \right\rangle_p \right] - N \sum_{s=s_0}^{r+p-1} (1-\delta_{rs}) b_{rs}(\ell_m) \left\langle \psi_{\ell_m}^{(s)} \right\rangle_{p-|r-s|}, \quad (3)$$

where the pointed brackets signify averages over the ion distribution function. The coefficients  $b_{rs}(\ell_m)$  are matrix elements of the linearized Boltzmann collision operator for multicomponent gas mixtures with respect to the  $\psi_{\ell_m}^{(r)}$ , and are defined and tabulated in Ref. [12-14]. Dependence on composition of the mixture is entirely in the  $b_{rs}(\ell_m)$ , which are linear in the mole fractions. The summation in the last term begins at  $s_0 = r-p+1$  or  $0$ , whichever is larger, and includes only those matrix elements less than  $p$  units off the diagonal.

The iteration begins at  $p=1$  by neglecting the terms in the summation and solving for  $\left\langle \psi_{\ell_m}^{(r)} \right\rangle_1$ , and then proceedings to  $p=2,3$ , etc. The mean power absorption  $\bar{A}$  from the electric field is the time average of

$$A(t) = nq \left\langle \underline{v}(t) \right\rangle \cdot \underline{E}(t) = nq E_0 \left\langle v_z(t) \right\rangle \sin \omega t. \quad (4)$$

Thus we must solve eq. (3) for  $\left\langle \psi_{10}^{(0)}(t) \right\rangle_p \equiv \left\langle c_z(t) \right\rangle_p$ . For  $p=1$  we obtain two coupled differential equations from eq. (3), and for  $p=2$  we obtain eight partially coupled differential equations. Solution of these increasingly large sets of differential equations leads to a series for  $\bar{A}$  in powers of  $(E/N)^2$ . The first iteration neglects all off-diagonal matrix elements and yields the usual Lorentzian line shape for  $\bar{A}$  [1,2]. This result will be exact for very weak electric fields, or for all electric fields if the off-diagonal matrix elements are zero. This is the case for the Maxwell model and the Rayleigh model,

which thus always give Lorentzian line shapes.

Deviations from Lorentzian line shape first appear in the second iteration, which yields

$$\bar{A} = \frac{nq^2 E_o^2}{4m\bar{v}} \left( \frac{1}{1 + \Omega^2} \right) \left[ 1 + \frac{c_1 c_2 \mathcal{E}^2}{(1 + \Omega^2)(c_2^2 + \Omega^2)} + O(\mathcal{E}^4) + \dots \right], \quad (5)$$

where  $\bar{v} \equiv Nb_{00}(10)$  is the zero-field mean collision frequency of the ions for momentum transfer to the neutrals in the mixture, and

$$\Omega = (\omega - \omega_c)/\bar{v}, \quad (6)$$

$$\mathcal{E} = (qE_o/m\bar{v}) (m/2kT)^{1/2}, \quad (7)$$

$$c_1 = \frac{5b_{01}(10)}{3b_{11}(00)} + \frac{b_{01}(10)}{6b_{00}(20)}, \quad (8)$$

$$c_2 = b_{11}(10)/b_{00}(10). \quad (9)$$

A physically interesting feature of the above formula is the occurrence of  $b_{01}(10)$ , which depends strongly on the nature of the ion-neutral force law. For ions in a single gas of mass  $M$  the expressions for  $c_1$  and  $c_2$  become

$$c_1 = -\frac{1}{12} (6C^* - 5) (M/m) (11m + 6MA^*) (5m + 3MA^*)^{-1}, \quad (10)$$

$$c_2 \approx (3m^2 + M^2 + \frac{8}{5} mMA^*) (m + M)^{-2}, \quad (11)$$

where  $C^*$  and  $A^*$  are conventionally defined [15] ratios of collision integrals. The crucial part coming from  $b_{01}(10)$  is the factor  $6C^* - 5$ , which also plays a crucial role in the theory of thermal diffusion in gases. Discussions of the relation of thermal diffusion to molecular collisions and force laws can therefore be taken over directly and applied to the relation between ion-neutral interactions and devia-

tions from Lorentzian line shape [16,17].

As an illustration of the effects on line shape of a repulsive ion-neutral force law, we consider the case of rigid spheres and equal masses ( $m=M$ ), for which  $c_1 = -17/96$  and  $c_2 = 7/5$ . The results are shown in fig. 1 for several values of  $\mathcal{E}$ . The line is Lorentzian for  $\mathcal{E} = 0$ , but the absorption is less for  $\mathcal{E} > 0$  because the effective collision frequency increases with increasing ion energy for repulsive potentials "harder" than  $r^{-4}$ . The effect is greatest at the line center because the ion energy is greatest at resonance. These results are qualitatively the same for any gas temperature.

For a more realistic ion-neutral interaction, such as a long-range attraction plus a short-range repulsion, the effective collision frequency has a more complicated dependence on field strength and gas temperature. For low gas temperatures the collision frequency may first decrease with increasing field strength, pass through a minimum, and then increase. For high gas temperatures it may increase from the beginning. The effect on the line shape is qualitatively illustrated in fig. 2. The qualitative effect can be inferred from the above considerations without explicit computations, just as the static field dependence of the ion mobility at a given gas temperature can be inferred from the temperature dependence of the zero-field mobility, as first discussed by Kihara [10,11,14].

The foregoing remarks can be made mathematically explicit by expressing the absorption line shape in terms of the ion mobility  $K$  in a static electric field. Eliminating  $\mathcal{E}^2$  between eq. (5) and the corresponding expression for  $K$  to the same order of approximation [11,12,14], we obtain

$$\bar{A} = \frac{nqE_0^2 K(0)}{4(1 + \Omega^2)} \left[ 1 + \frac{c_2^2 c_3}{24(1 + \Omega^2)(c_2^2 + \Omega^2)} \frac{d \ln K}{d \ln (E_0/N)} + \dots \right], \quad (12)$$

where  $K(0)$  is the zero-field limit of the mobility, so that

$\Omega = (\omega - \omega_c) q/mK(0)$ , and

$$c_3 = 3 \left[ b_{11}(00) + 10b_{00}(20) \right] / \left[ 4b_{11}(00) + 5b_{00}(20) \right], \quad (13)$$

which for single gases reduces to  $c_3 = (11m + 6MA^*)/(3m + 4MA^*)$ .

Both  $c_2$  and  $c_3$  are virtually independent of the ion-neutral force law, which enters only weakly through  $A^*$ . As written, eqs. (12) and (13) are valid for multicomponent mixtures of neutral gases.

### 3. Discussion

Since ICR lines are often used as a probe for chemical analysis [18], it is important to note that  $\bar{A}$  remains proportional to  $\underline{n}$  even when the line shape is non-Lorentzian.

Since the present results give  $\bar{A}$  as a function of  $\Omega^2$ , the line shape is predicted to be symmetric about  $\Omega = 0$ . Skewness of line shape [19] therefore cannot be attributed to the nature of the ion-neutral force law. A similar remark applies to the central dips sometimes seen in ICR lines.

The convergence of the expansion in  $\mathcal{E}^2$  may be slow, and eq. (12) is likely to have a much larger range of usefulness than eq. (5), if one judges by the analogous expressions for static-field ion mobility and diffusion [12].

The fundamental limitations of the present theory are  $n \ll N$  and elastic collisions. The other restrictions are readily removable in principle, the cost being only mathematical complexity.

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Figure Captions

Fig. 1. Reduced ICR absorption  $\bar{A}(\Omega, \mathcal{E})$  as a function of  $\Omega = (\omega - \omega_c)/\bar{\nu}$  for several values of reduced electric field strength  $\mathcal{E}$ , for the model of rigid spheres of equal mass ( $m = M$ ). The curve is Lorentzian for  $\mathcal{E} = 0$ .

Fig. 2. Qualitative behavior of  $\bar{A}(\Omega, \mathcal{E})$  for a potential consisting of a rigid sphere with long-range attraction. The plots are made for  $\mathcal{E} = 1$  at several gas temperatures. The curve for  $T = \infty$  is the same as the curve for  $\mathcal{E} = 1$  in fig. 1.



